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Applicant: NIPPON OIL CO. LTD.
3-12, Nishi Shinbashi 1-chome
Minato-ku Tokyo(JP)

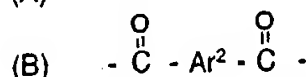
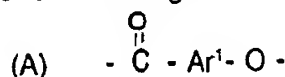
Inventor: Kaminade, Tadahiro
17-25 Shinjoanka-machi
Kawasaki-shi, Kanagawa-ken(JP)

Inventor: Toya, Tomohiro
1178 Shinbashi-cho, Izumi-ku
Yokohama-shi, Kanagawa-ken(JP)
Inventor: Iida, Shigeki
155-72 Honmokuosato-cho, Naka-ku
Yokohama-shi, Kanagawa-ken(JP)
Inventor: Hara, Hajime
4-5-11 Kugenumafujigaya
Fujisawa-shi, Kanagawa-ken(JP)

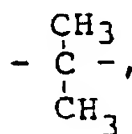
Representative: Cropp, John Anthony David et
al
MATHYS & SQUIRE 10 Fleet Street
London, EC4Y 1AY(GB)

Wholly aromatic polyesters.

Provided is a wholly aromatic polyester superior in melt processability and tenacity which consists essentially of the following structural units (A), (B) and (C) and wherein 0.2 to 40 mole% of the total of said units are of ortho configuration;



(C) $- \text{O} - \text{Ar}^2 \{ \text{Z}_m - \text{Ar}^1 \}_n - \text{O} -$ where Ar¹ and Ar² each represent a divalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the hydrogen atoms of said aromatic hydrocarbon group may be substituted with a halogen atom, an alkyl or alkoxy group having 1 to 4 carbon atoms, or phenyl; Z is



- O -, or -SO₂-; m is 0 or 1, at least 60 mole% of Ar¹ being constituted by a group selected from 1,4-phenylene, substituted 1,4-phenylenes, naphthyl and 4,4'-biphenyl.

EP 0 380 286 A2

Wholly Aromatic Polyesters

Background of the invention

The present invention relates to wholly aromatic polyesters, particularly wholly aromatic polyesters superior in melt processability and tenacity.

5 Recently there has been an increasing demand for upgrading of organic, high molecular materials so that there can be obtained fibers, films and moldings superior in mechanical properties such as tensile strength and modulus and in heat resistance.

As a high molecular material which satisfies the above demand there is known a rigid-rod polymer wherein only aromatic rings are linked together in the form of a straight chain. But this polymer is very poor
10 in its solubility to solvents and the melting point thereof is very high. For this reason it has been difficult to effect processing in the state of a solution or in a melted state.

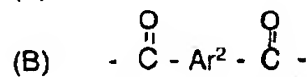
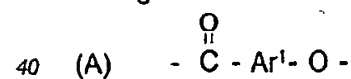
For solving the above problem there have been proposed a method of introducing an aliphatic chain in the main chain, a method of introducing therein an m-substituted compound, a method of introducing therein a 2,6-substituted naphthalene ring, and a method of introducing in an aromatic ring a bulky
15 substituent such as alkyl, halogen, or phenyl. Since the melting point can be lowered by these methods, it becomes possible to effect melt molding, and particularly in a liquid crystal phase, the fluidity is improved and so it becomes easy to perform molding. As typical examples of prior art publications disclosing polymers which exhibit such melt anisotropy there are mentioned Japanese Patent Publications Nos. 47870/1972 and 482/1980, 18016/1981 and 13531/1984 as well as Japanese Patent Laid-Open
20 Nos.65421/1978, 77691/1979, 144024/1980, 172921/1982, 69199/1979 and 25354/1982.

In those methods, however, there remain many problems to be solved. In the case where an aliphatic chain is copolymerized with the main chain, the resulting polymer is inferior in its mechanical properties and the heat resistance is impaired markedly. Also in the introduction of a m-substituted compound by copolymerization, the mechanical properties of the resulting copolymer are not always satisfactory and the
25 tenacity is impaired. The method of introducing a 2,6-substituted naphthalene ring can afford superior mechanical properties, but the retention of strength at high temperatures is not satisfactory and the monomer is expensive. The method of introducing a bulky substituent is also disadvantageous in that the retention of strength at high temperatures is not satisfactory and the monomer is expensive.

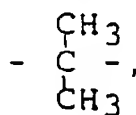
It is the object of the present invention to provide a wholly aromatic polyester capable of being
30 subjected to melt molding and superior in tenacity such as high impact resistance while having superior heat resistance.

Summary of the invention

35 The present invention resides in a wholly aromatic polyester consisting essentially of the following structural units (A), (B) and (C) and wherein 0.2 to 40 mole% of the total of said units are of ortho configuration:



(C)
$$- \text{O} - \text{Ar}^2 \{ \text{Z}_m - \text{Ar}^2 \}_n \text{O} -$$
 where Ar^1 and Ar^2 each represent a divalent aromatic hydrocarbon group having 6 to 20 carbon atoms, the hydrogen atoms of the said aromatic hydrocarbon group may be
45 substituted with a halogen atom, an alkyl or alkoxy group having 1 to 4 carbon atoms, or phenyl; Z is



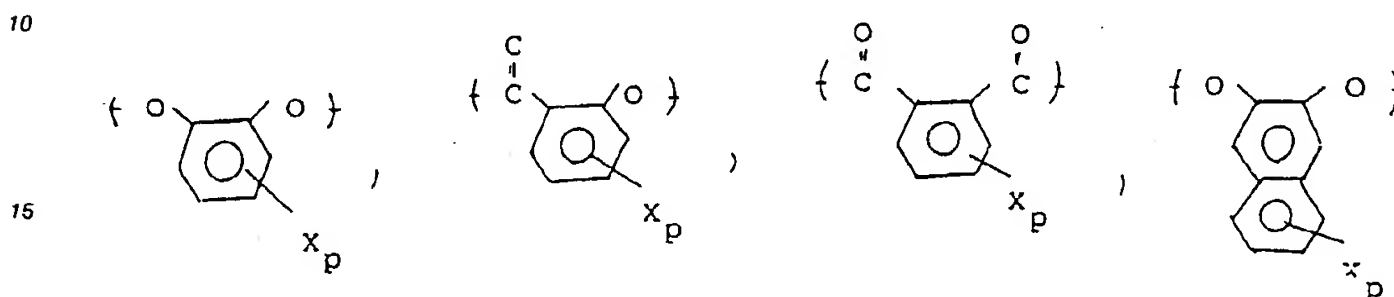
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- O -, or - SO₂ -; m is 0 or 1; and n is 0 or 1, at least 60 mole% of Ar^1 being constituted by a group selected from 1,4-phenylene, substituted 1,4-phenylenes, naphthylene and 4,4'-biphenyl.

Detailed Description of the Invention

As examples of Ar1 and Ar2 there are mentioned 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, substituted 1,4-phenylenes such as 2-chloro-1,4-phenylene, 2-fluoro-1,4-phenylene, 2-methyl-1,4-phenylene, 2-ethyl-1,4-phenylene, 2-[tert-butyl]-1,4-phenylene, 2-methoxy-1,4-phenylene, 2-ethoxy-1,4-phenylene, 2-phenyl-1,4-phenylene and 2,6-dimethyl-1,4-phenylene, 1,2-naphthylene, 1,4-naphthylene, 1,5-naphthylene, 2,6-naphthylene, and 4,4'-biphenyl.

The "structural unit of ortho configuration" in the present invention means a structural unit typified by the following:



wherein X represents a substituent group and p is 0 to 2.

The structural unit (A) is derived from an aromatic hydroxycarboxylic acid or a derivative thereof (e.g. acetylated derivative), and it is present in an amount in the range of 1 to 99 mole%, preferably 10 to 90 mole%, more preferably 30 to 70 mole%, of all the structural units in the polyester.

The structural unit (B) is derived from an aromatic dicarboxylic acid or a derivative thereof (e.g. dimethyl ester), and it is present in an amount in the range of 5 to 50 mole%, preferably 10 to 40 mole%, of all the structural units in the polyester.

The structural unit (C) is derived from an aromatic diol or a derivative thereof (e.g. diacetylated derivative), and it is present in an amount in the range of 5 to 50 mole%, preferably 10 to 40 mole%, of all the structural units in the polyester. The structural units (B) and (C) are present in a substantially equal number of moles in the polyester.

It is essential in the present invention that 0.2-40 mole%, preferably 1-30 mole%, more preferably 2-20 mole% of the total of said units are of ortho configuration. This is an essential condition for obtaining a wholly aromatic polyester capable of being subjected to melt molding and superior in tenacity while having superior heat resistance. If the proportion of the structural unit of ortho configuration is less than 0.2 mole%, it will be less effective in improving tenacity, while if it is more than 40 mole%, the resulting polyester will not exhibit melt anisotropy and its mechanical properties will be poor.

As suitable examples of compounds which afford the structural unit (A) there are mentioned p-hydroxybenzoic acid, m-hydroxybenzoic acid, salicylic acid, 4-hydroxy-3-chlorobenzoic acid, 4-hydroxy-3-methylbenzoic acid, 4-hydroxy-3,5-dimethylbenzoic acid, 2-hydroxy-6-naphthoic acid, 1-hydroxy-5-naphthoic acid, 1-hydroxy-4-naphthoic acid, syringic acid, vanillic acid, and 4-hydroxy-4'-biphenylcarboxylic acid. These compounds may be used alone or as a mixture of two or more. For maintaining melt anisotropy, it is necessary that at least 60 mole%, preferably not less than 80 mole%, of Ar1 contain a linear chain extension bond selected from 1,4-phenylene, substituted 1,4-phenylenes, 2,6-naphthyl and 4,4'-biphenyl.

As suitable examples of compounds which afford the structural unit (B) there are mentioned terephthalic acid, methoxyterephthalic acid, ethoxyterephthalic acid, fluoroterephthalic acid, chloroterephthalic acid, methylterephthalic acid, isophthalic acid, phthalic acid, methoxyisophthalic acid, diphenyl-4,4'-dicarboxylic acid, naphthalene-2,6-dicarboxylic acid, naphthalene-1,5-dicarboxylic acid, naphthalene-1,4-dicarboxylic acid, and naphthalene-1,2-dicarboxylic acid. These compounds may be used each alone or as a mixture of two or more.

As suitable examples of compounds which afford the structural unit (C) there are mentioned hydroquinone, catechol, resorcinol, methylhydroquinone, chlorohydroquinone, phenylhydroquinone, 1,2-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,2'-bis(4-hydroxyphenyl)propane, 4,4'-biphenol, 4,4'-dihydroxydiphenyl ether, and 4,4'-dihydroxydiphenyl sulfone. These compounds may be used alone or as a mixture of two or more.

The polyester of the present invention can be prepared by any of various ester forming reactions, but usually it is prepared by melt polymerization. Preferably there is adopted a method in which starting compounds which afford the structural units (A) and (C) are fed after conversion of their hydroxyl groups

into the form of a lower alkyl ester and a polycondensation reaction is allowed to proceed by an ester interchange reaction. As the lower alkyl ester, acetate is most preferred.

The polycondensation reaction will proceed even in the absence of catalyst, but the use of a known ester interchange catalyst is preferable in order to accelerate polymerization. The catalyst may be used in an amount in the range of 0.001 to 1 wt%, preferably 0.005 to 0.5 wt% of the total monomer weight. Examples of such catalyst include alkali metal carboxylates, alkaline earth metal carboxylates, alkyltin oxides, diaryltin oxides, alkylstannic acids, titanium dioxide, alkoxytitanium silicates, titanium alkoxides, Lewis acids, and hydrogen halides.

The melt polymerization is performed at a temperature in the range of usually 150° to 375° C, preferably 200° to 350° C, in an inert gas atmosphere such as nitrogen or argon, under passing of the said gas, or under reduced pressure. As the polymerization proceeds, acetic acid will be distilled out in the case of using acetate monomers, so according to the amount thereof distilled out and the polymer viscosity the reaction temperature is raised and the degree of pressure reduction is adjusted. The polymerization time is usually in the range of 1 to 10 hours. After completion of the melt polymerization the polymer may be pulverized finely and the polymerization may be further proceeded in solid phase at a temperature below the melting point of the polymer to increase the degree of polymerization.

The polyester of the present invention exhibits an inherent viscosity of 0.5 to 10 dL/g, preferably, 1 to 7 dL/g as determined at 60° C at a concentration of 0.1 wt/vol % in pentafluorophenol. If its inherent viscosity is lower than 0.5 dL/g, the polyester will be too small in molecular weight and inferior in mechanical properties, while if its inherent viscosity is higher than 10 dL/g, it will become difficult for the polyester to be subjected to melt processing.

The inherent viscosity, η_{inh} , is calculated as follows:

$$\eta_{inh} = \frac{\ln t/t_0}{c}$$

t_0 : dropping time of pentafluorophenol as a solvent as determined at 60° C using a Ubbelohde's viscometer

t : dropping time of a solution of a sample dissolved therein

c : concentration of the sample (g/dL)

By a conventional melt molding method the polyester of the present invention can be formed into films, sheets, injection moldings and various other moldings. As compared with moldings obtained from conventional thermotropic liquid crystalline polyesters, the moldings obtained from the polyester of the present invention are superior in elongation at break and tenacity, so it is possible to make the most of the characteristic features of the polyester of the invention in its use as films, sheets, or moldings.

The present invention will be described below in terms of examples thereof, but it is to be understood that the invention is not limited thereto.

Example 1

A polymerization example will be described below, in which catechol was used as a monomer affording the structural unit of ortho configuration and formed 2.5 moles % of the total monomer units.

4.0 moles (720 g) of p-acetoxybenzoic acid, 2.0 moles (332 g) of terephthalic acid, 1.81 moles (489 g) of biphenol diacetate and 0.20 mole (39 g) of catechol diacetate were fed into a 3-liter autoclave equipped with a stirrer, a gas inlet, a distillation head and a reflux condenser. Then, the autoclave was evacuated to vacuum and purged with nitrogen. On heating to 100° C in a nitrogen atmosphere stirring was started. After holding 0.5 hour at each of 100°, 130°, 150° and 180° C, the temperature was raised to 200° C. Then, from 200° C up to 330° C heating was continued with stirring at a rate of 30° C/hr while acetic acid was distilled off. The resulting polymer was then withdrawn, solidified and thereafter pulverized. The polymer thus pulverized was subjected to a solid-phase polymerization in a vacuum of 1 mmHg in a rotary evaporator at 180° C for 0.5 hour, 220° C for 1 hour, 240° C for 1 hour, 250° C for 1 hour, 260° C for 1 hour, 270° C for 1 hour and 280° C for 6 hours. The resulting polymer exhibited an inherent viscosity of 3.3 dL/g as measured at 60° C at a concentration of 0.1 wt/vol % in pentafluorophenol.

When the polymer was subjected to a thermal analysis at the heat-up rate of 20° C/min using a differential scanning calorimeter (DSC), an endothermic peak was observed at 362° C. Further, using a hot stage, the polymer in a melted state was observed by means of a polarizing microscope under a crossed

nicol. As a result, the polymer exhibited melt anisotropy optically.

A test piece obtained by injection molding of the polymer after the solid-phase polymerization was measured for bending strength and bending modulus according JIS K7203 and also measured for notched Izod impact strength according to JIS K7110. The results are as shown in Table 1.

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Example 2

A polymerization example will be described below, in which catechol was used as a monomer affording the structural unit of ortho configuration and formed 6.2 mole % of the total monomer units.

According to the method used in Example 1, 4.0 moles (720 g) of p-acetoxybenzoic acid, 2.0 moles (332 g) of terephthalic acid, 1.51 moles (407 g) of biphenol diacetate and 0.5 mole (98 g) of catechol diacetate were fed and polymerization was conducted. Provided, however, that after reaching 330°C, the polymer was held at the same temperature for 1 hour and then withdrawn. The polymer after pulverized was subjected to a solid-phase polymerization in the same manner as in Example 1 to afford a polymer having an inherent viscosity of 3.9 dL/g. In the DSC measurement, the polymer was found to have a melting point of 341°C, and it exhibited melt anisotropy optically. Mechanical properties of a molded product obtained from this polymer are as shown in Table 1.

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Example 3

A polymerization example will be described below, in which catechol was used as a monomer affording the structural unit of ortho configuration and was fed 12.5 mole%.

According to the method used in Example 1, 4.0 moles (720 g) of p-acetoxybenzoic acid, 2.0 moles (332 g) of terephthalic acid, 1.01 moles (270 g) of biphenol diacetate and 1.0 mole (194 g) of catechol diacetate were fed and polymerization was conducted. Provided, however, that after reaching 330°C, the polymer was held at the same temperature for 2 hours and then withdrawn. The polymer after pulverization was subjected to solid-phase polymerization in the same manner as in Example 1 to afford a polymer having an inherent viscosity of 4.1 dL/g. In the DSC measurement the polymer did not exhibit a clear melting point, but at temperatures not lower than about 300°C it exhibited melt anisotropy optically. Mechanical properties of a molded product obtained from the polymer are as shown in Table 1.

Example 4

A polymerization example will be described below, in which salicylic acid was used as a monomer affording the structural unit of ortho configuration and formed 6.2 mole% of the total monomer units.

According to the method used in Example 1, 3.5 moles (630 g) of p-acetoxybenzoic acid, 0.5 mole (90 g) of acetylsalicylic acid, 2.0 moles (332 g) of terephthalic acid and 2.01 moles (543 g) of biphenol diacetate were fed and polymerization was conducted. Provided, however, that after reaching 330°C, the polymer was held at the same temperature for 1 hour and then withdrawn. The polymer after pulverization was subjected to a solid-phase polymerization in the same way as in Example 1 to afford a polymer having an inherent viscosity of 3.5 dL/g. In the DSC measurement the polymer was found to have a melting point of 345°C, and it exhibited melt anisotropy optically. Mechanical properties of a molded product obtained from the polymer are as shown in Table 1.

Example 5

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A polymerization example will be described below, in which catechol was used as a monomer affording the structural unit of ortho configuration and formed 6.2 mole % of the total monomer units.

According to the method used in Example 1, 4.0 moles (720 g) of p-acetoxybenzoic acid, 2.0 moles (332 g) of terephthalic acid, 1.51 moles (296 g) of hydroquinone diacetate and 0.5 mole (98 g) of catechol diacetate were fed and polymerization was conducted. Provided, however that after reaching 330°C, the polymer was held at the same temperature for 0.5 hour and then withdrawn. The polymer after pulverization was subjected to a solid-phase polymerization in the same way as in Example 1 to afford a polymer having an inherent viscosity of 3.9 dL/g. In the DSC measurement the polymer was found to have a melting point

of 350° C and exhibited melt anisotropy optically. Mechanical properties of a molded product obtained from the polymer are as set forth in Table 1.

5 Comparative Examples 1 - 3

In place of catechol diacetate of Examples 1-3 there was used isophthalic acid as a monomer component for disarranging the linearity of the polymer chains to lower their melting points. Monomer compositions are as tabulated below.

	p-Acetoxybenzoic acid (mole)	Terephthalic acid (mole)	Isophthalic acid (mole)	Biphenyl diacetate (mole)
Comp. Ex. 1	4.0	1.8	0.2	2.01
Comp. Ex. 2	4.0	1.5	0.5	2.01
Comp. Ex. 3	4.0	1.0	1.0	2.01

Polymerizations and solid-phase polymerizations were performed according to the respective corresponding Examples 1-3. The following table shows melting points of the resulting polymers determined from endothermic peaks observed in the DSC measurement, as well as inherent viscosities of the polymers. All of the polymers exhibited melt anisotropy.

	m. p. (°C)	η_{inh} (dl/g)
Comp. Ex. 1	383	could not be determined, because of poor solubility.
" 2	358	3.2
" 3	325	4.2

Mechanical properties of molded products obtained from the polymers are as set forth in Table 1.

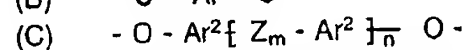
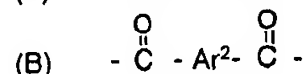
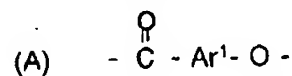
Table 1

	Monomer component disarranging linearity (mole %)	Mechanical Properties of Molded Product		
		Bending Strength (kg/cm ³)	Bending Modulus (kg/cm ²)	Notched Izod Impact Strength (kg.cm/cm)
Ex.1.	catechol(2.5)	1.75X10 ³	13.5X10 ⁴	35
2.	catechol(6.25)	1.66X10 ³	10.0X10 ⁴	38
3.	catechol(12.5)	1.46X10 ³	11.2X10 ⁴	90
4.	salicylic acid(6.25)	2.01X10 ³	9.0X10 ⁴	50
5.	catechol(6.25)	1.33X10 ⁴	9.8X10 ⁴	44
Comp.Ex.1.	isophthalic acid(2.5)	1.40X10 ³	12.6X10 ⁴	20
2.	isophthalic acid(6.25)	1.03X10 ³	6.5X10 ⁴	15
3.	isophthalic acid(12.5)	1.38X10 ³	8.7X10 ⁴	55

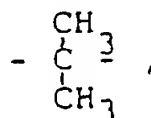
According to the present invention, as set forth above, there is provided a wholly aromatic polyester superior in tenacity such as strength and impact resistance while retaining high heat resistance.

Claims

1. A wholly aromatic polyester consisting essentially of the following structural units (A), (B) and (C) and wherein 0.2 to 40 mole% of the total of said units are of ortho configuration;



where Ar^1 and Ar^2 each represent a divalent aromatic hydrocarbon group having 6 to 20 carbon atoms or a substituted derivative thereof wherein one or more of the hydrogen atoms is substituted with a halogen atom, an alkyl or alkoxy group having 1 to 4 carbon atoms, or phenyl; Z is



- O -, or - SO_2 -; m is 0 or 1; and n is 0 or 1, at least 60 mole% of Ar^1 being constituted by a group selected from 1,4-phenylene, substituted 1,4-phenylenes, naphthyl and 4,4'-biphenyl.

2. A wholly aromatic polyester as set forth in Claim 1, containing the structural units (A), (B) and (C) in the proportions of 1-99 mole%, 5-50 mole% and 5-50 mole%, respectively, the structural units (B) and (C) being present in substantially equimolar proportions.

3. A wholly aromatic polyester as set forth in Claim 1 or Claim 2 wherein Ar^1 and Ar^2 are independently selected from 1,2-phenylene, 1,3-phenylene, 1,4-phenylene, 2-chloro-1,4-phenylene, 2-fluoro-1,4-phenylene, 2-methyl-1,4-phenylene, 2-ethyl-1,4-phenylene, 2-[tert-butyl]-1,4-phenylene, 2-methoxy-1,4-phenylene, 2-ethoxy-1,4-phenylene, 2-phenyl-1,4-phenylene and 2,6-dimethyl-1,4-phenylene, 1,2-naphthylene, 1,4-naphthylene, 1,5-naphthylene, 2,6-naphthylene, and 4,4'-biphenyl.

4. A wholly aromatic polyester as set forth in any one of Claims 1, 2 or 3 wherein said structural unit (C) is derived from hydroquinone, catechol, resorcinol, methylhydroquinone, chlorohydroquinone, phenylhydroquinone, 1,2-dihydroxynaphthalene, 1,4-dihydroxynaphthalene, 2,6-dihydroxynaphthalene, 2,2'-bis(4-hydroxyphenyl)propane, 4,4'-biphenol, 4,4'-dihydroxydiphenyl ether or 4,4'-dihydroxydiphenyl sulfone.